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NATIONAL BUREAU OF STANDARDS WASHINGTON DC QUANTUM CH--ETC F/G 20/5
THEORETICAL STUDIES OF ELECTRONIC TRANSITION LASERS.(U)
1979 M KRAUSS, W J STEVENS

N00014-79-F-0043

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Annual Report to FY 1979

Theoretical Studies of Electronic Transition Lasers.

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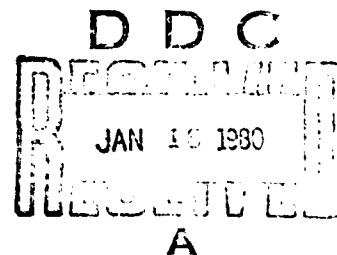
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Introduction

Self-absorption in electronic transition lasers can severely limit the efficiencies of such systems. We identified a bound-continuum X-A as well as possible bound-bound transitions which could absorb at the B-X lasing energy in Group II b-halides. Figure 1 shows the bound-continuum absorption transition for HgCl. Experimental evidence for these transitions is non-existent and ab initio calculations are required to obtain the spectroscopic properties of these systems. We can note parenthetically that the determination of the energies and spectroscopic properties of excimer and ion-pair type electronic transition lasers has relied heavily on ab initio calculation.

A well-defined calculation scheme has been developed which is applicable over the entire periodic table. Relativistic λ -dependent pseudopotentials have been used in the calculation of the electronic structure and transition moments of HgCl. Compact but accurate bases have been determined variationally at the double zeta plus polarization level. The final wave functions, energies, and properties have been obtained at the first-order configuration interaction level of accuracy. Because pseudopotentials are used, the paraphernalia of computing the wavefunctions such as trial inputs and configuration interaction formula tapes are identical for all Group II b-halides, which would permit straight-forward extension of the HgCl results. Using general Franck-Condon codes that calculate bound-bound, bound-continuum, and continuum-continuum transitions from the theoretically computed energy and transition moment curves, we have calculated the photodissociation cross section for the HgCl

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$X^2\Sigma^+ - A^2\Pi$ transition, shown in Fig. 2, as a function of the transition energy.

A preliminary analysis of the energetics of the excimer states for the rare gas halides has also been made. Weak radiative transitions play several roles in this case. They provide diagnostics or can be used to photodissociate or pump higher states. In addition, the presence of the $B \rightarrow A$ radiative transition complicates the analysis of the kinetic data with regard to both the relative B and C energies and the quenching of these states.

Four notes have been published or submitted to date. Titles and abstracts are listed below. We greatly benefited from the assistance of guest workers from the Chemistry Department of SUNY, Binghamton, M. E. Rosenkrantz and D. D. Konowalow. A paper on the "The Electronic Structure and Spectroscopy of the X, A, and B States of HgCl" is in preparation.

The abstracts provide a summary of our conclusions. The self-absorption calculations on HgCl are completed. Questions still remain concerning the ordering of the B and C states in the rare-gas halides. During FY80 we will extend our calculations to the rare gas halide triatomic systems in order to estimate the role of these species in the kinetics and radiative properties of high pressure rare-gas halide laser mixtures. Photodissociation calculations of the $X \rightarrow A$ transitions in the diatomic rare gas-halide molecules will also be used to probe problems in the temperature dependence of the efficiency for systems with significantly bound X states.

II. Titles and Abstracts

1. Photodissociation of HgCl
P. S. Julianne, D. D. Konowalow, M. Krauss, M. E. Rosenkrantz,
W. J. Stevens
To be published Applied Physics Letters.

Transition moments and energies have been calculated for the X-A, bound to continuum, transition in HgCl. The photodissociation cross section at the peak is $1.2 \times 10^{-18} \text{ cm}^2$ at 600K. The laser energy for the B-X transition is close to the peak energy and a significant absorption will result from a buildup in the concentration of X state HgCl in the course of exciting the laser media. The absorption is suggested as an explanation for the low extraction efficiencies observed for HgCl lasers.

2. Dipole Polarizabilities of Zn, Cd, and Hg (1S).
D. D. Konowalow, M. E. Rosenkrantz, W. J. Stevens, and M. Krauss
Chem. Phys. Lett. 64, 317 (1979).

Effective core potentials (ECP) are used in a calculation of the dipole polarizability of the ground states of the Zn, Cd, and Hg atoms. The trend in the magnitude of the polarizability as a function of increasing Z of the recommended values is reproduced in the calculated polarizabilities using relativistic ECP. Polarizabilities obtained with non-relativistic ECP do not reflect the observed trend and are much too large in magnitude.

Compact atomic bases, useful for molecular calculations, are obtained by optimization of the function exponents with respect to both the energy and polarizability.

3. Dipole Polarizabilities of the Group II b-Atoms Obtained From Compact Variational Trial Functions.
M. E. Rosenkrantz, W. J. Stevens, M. Krauss, and D. D. Konowalow
To be published J. Chem. Phys.

In order to optimize basis sets for future molecular calculations, the energies and dipole polarizabilities of 1S , 3P , and 1P states of Zn, Cd, and Hg have been determined from Hartree-Fock (HF) and multi-configuration calculations. These utilize either empirically fitted pseudopotentials or ab initio effective core potentials (ECP). Our calculated polarizabilities for ground state atoms agree within 10% with recommended values so long as either the empirical pseudopotentials or the ECP based on relativistic HF calculations are used. Our calculations agree with the measured anisotropy of the polarizability of 3P_1 Hg, but disagree with measured values of the 3P_2 state anisotropy. Our calculated 3P_2 anisotropy is consistent with both the measured and calculated 3P_1 Hg anisotropy; the measured 3P_2 values are not. We find calculations based on non-relativistic ECP to give incorrect polarizabilities.

4. Role of the III $1/2$ - II $1/2$ Transition in Rare Gas Halide Kinetics.
P. S. Julianne and M. Krauss
Applied Physics Letters 35, 55 (1979).

Rare gas halide spectra have previously been analyzed in terms of the strong III $1/2$ - I $1/2$ lasing transition and the weaker II $3/2$ - I $3/2$ broad continuum. However, the III $1/2$ - II $1/2$ transition is also a broad continuum that strongly overlaps the II $3/2$ - I $3/2$ transition and has an Einstein coefficient of a similar magnitude. The existence of this transition requires a reinterpretation of previous kinetic data on ArF, KrF, XeF. Simultaneous energy extraction from both the III $1/2$ and II $3/2$ states should be possible for lasing in the broad continuum.

